

Formation of Solid Electrolyte Interface on Cycled Lithium-ion Battery Cathodes

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Beamline(s): U7A

Introduction: Lithium-ion batteries are promising candidates for hybrid electric vehicles (HEV). Batteries that exceed the requirements for HEV, as set by the Partnership for a New Generation of Vehicles (PNGV), have been designed and built. These batteries are based on thin $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ cathodes, thin carbonaceous anodes, and a 1 M LiPF_6 ethylene carbonate (EC): diethyl carbonate (DEC) (1:1) electrolyte. A major technical barrier is that the batteries lose their high power capability during use or prolonged storage, particularly at elevated temperatures. Electrochemical impedance spectroscopy indicates that the power fade is due to an increase in cathode impedance in cycled and abused cells. X-ray diffraction and hard X-ray absorption spectroscopy clearly shows that the bulk of the cathode material is largely intact. It is conceivable that the power fade is related to electrolyte decomposition products that are formed on the surface of the cathode. The decomposition products form the solid electrolyte interface (SEI) and might affect ionic motion by pore plugging, or could contribute to resistive electrical paths to parts of the cathode structure. Although the presence of a SEI on the cathode has long been suspected, confirmation of such a layer has proved elusive. In order to study the nature of the SEI layer it is important to use structural techniques with some surface sensitivity. We have explored the use of soft X-ray absorption spectroscopy to study the nature of the SEI layers in lithium-ion battery cathodes.

Methods and Materials: Soft x-ray absorption measurements were performed at U7A on cathodes extracted from cycled and abuse-tested cells. Ni and Co L_3 and L_2 edges as well as oxygen and fluorine K edges were recorded, all having energies between 500 and 900 eV. These measurements, obtained in the electron yield mode, sampled to a depth of $\sim 5\text{nm}$.

Results: XAS at the F K-edge demonstrates the presence of LiF in addition to poly(vinylidene fluoride) (PVdF) on the surface of cycled and abused electrodes. PVdF is a binder added to the cathode and is an essential component of the cathode assembly. The results indicate that the PVdF in the cycled electrodes is largely intact and that the LiF comes from decomposition of LiPF_6 from the electrolyte. The precipitated LiF is the most likely major contributor to the insulating layer found on cycled and abused electrodes. The nature of the LiF coating and its contribution to power fade will be the subject of further studies. Our investigation suggests that XAS is a valuable surface chemistry tool in the study of SEI formation at the cathode.

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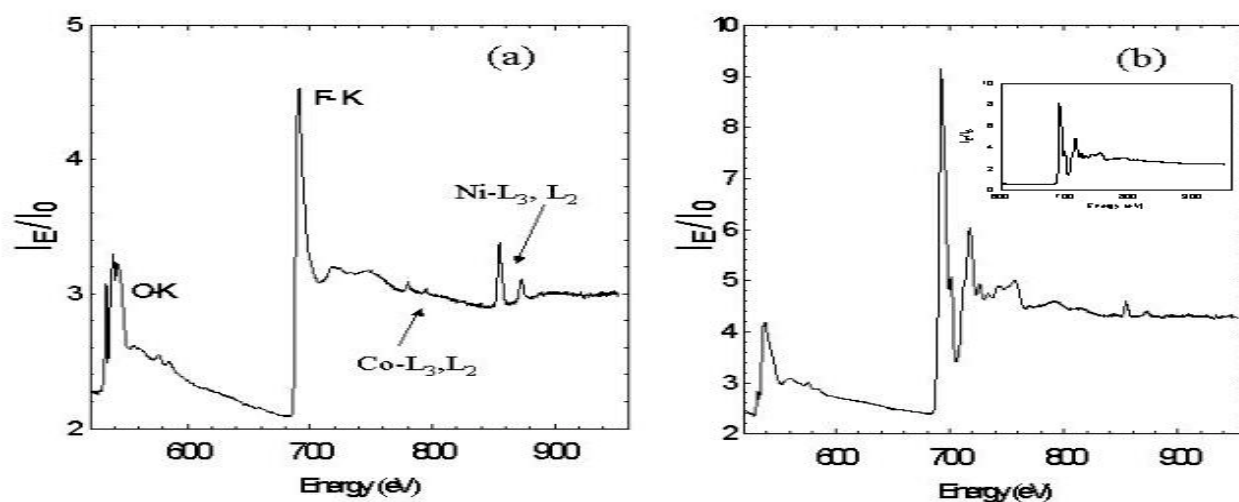


Figure 1. Soft x-ray absorption in the electron yield mode, for (a) an as prepared cathode electrode and (b) for an electrode subjected to cycling and abuse testing. Note the major changes at the F K edge (in the region of 690 – 750 eV) due to the formation of LiF. Figure 1 (a) indicates the sources of the various features of the spectra. The inset in Fig. 1 (b) shows the F K-edge XAS of LiF.